ME 5329 Assignment 5

Potential Energy Surface of H_2CO Using Nudged Elastic Band (NEB) Transition State Algorithm

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Dr. Aquino Fall 2025

Objectives:

- Learn about Nudged Elastic Band (NEB) Transition State Algorithm.
- Learn about how to find a transition state and why it is important to characterizing the kinetics of a reaction.
- Learn about the Zero Point Energy (ZPE) Correction and how it affects reaction energies.

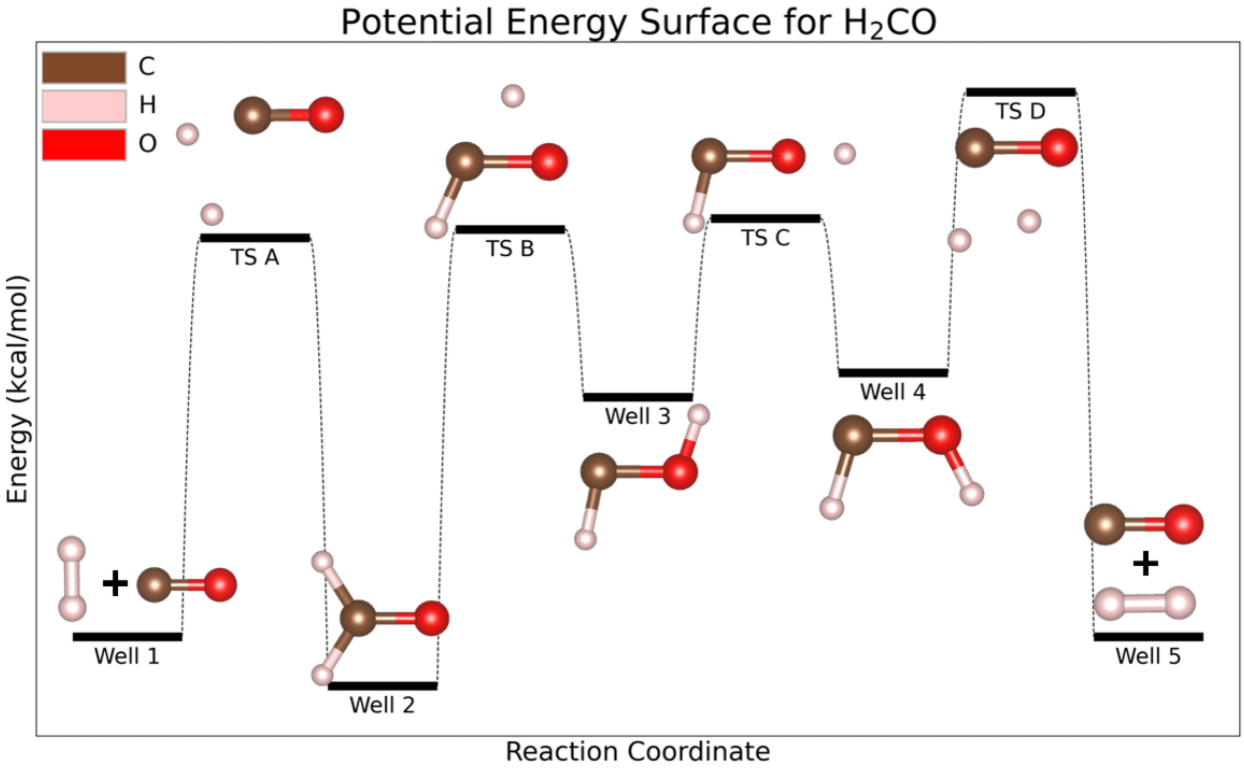

Figure 1: Visualized Potential Energy Surface of H_2CO

Description of the Potential Energy Surface of H_2CO:

1. By using ORCA we are going to characterize the reaction pathway shown in Figure 1. Each reaction to be characterized is described below:

   - Reaction A: $H_2 + CO \longleftrightarrow H_2CO$
   - Reaction B: $H_2CO \longleftrightarrow$ HCOH (anti)
   - Reaction C: HCOH (anti) $\longleftrightarrow$ HCOH (syn)
   - Reaction D: HCOH (syn) $\longleftrightarrow H_2 + CO$

2. Below are names for each minima/well:

   - Well 1 and Well 5: Hydrogen gas (H_2) and carbon monoxide (CO)
   - Well 2: Formaldehyde (H_2CO)
   - Well 3: Anti-hydroxymethylene (HCOH)
   - Well 4: Syn-hydroxymethylene (HCOH)

3. A Note on Chemistry Terminology:

   - The terms **anti** or **antiperiplanar** refers to when the H−C−O−H dihedral angle in hydroxymethylene is approximately 180 °. Similarly, **syn** or **synperiplanar** refer to when this dihedral angle is approximately 0 °. In other words, the anti conformer has the two hydrogens on opposite sides of the molecule, while the syn conformer has the hydrogens on the same side. This difference in dihedral angle is important because it can affect the molecule's reactivity.
   - An **isomer** is a molecule that has the same molecular formula as another but differs in the connectivity or spatial arrangement of its atoms. Hydroxymethylene is an isomer of formaldehyde. We say it this way because formaldehyde is stable and hydroxymethylene is unstable.
   - Hydroxymethylene is also called a **tautomer** of formaldehyde, which is a special type of isomer that differs in the position of a proton and the location of a double bond.
   - The specific isomer of a molecule can be very important in biology and medicine. A famous example is the drug **Thalidomide**, where one enantiomer (a mirror-image isomer) was used to treat morning sickness in pregnant women, while the other enantiomer caused severe birth defects in the 1950s and 1960s.

Instructions:

1. Create each well structure found in the potential energy surface we are calculating. You may use SMILE strings or a Python script generating with a reasonable guess for species bond lengths and bond angles. For Well 1 and Well 5, create a reasonable structure containing CO and H_2 in one .xyz file with a CH distance of ~ 5Å.

2. For each well structure, do an ORCA geometry optimization using KS-DFT functional B3LYP and basis set 6-31G* and calculate the vibrational frequencies of the optimized structure using ORCA.The charge of each system is 0 and the multiplicity of this system is 1.

3. Use the nudged elastic band (NEB) algorithm in ORCA to find the transition state (TS) for each reaction on the potential energy surface.

   - To do this, you take the initial optimized well geometry (`initial_well_opt.xyz`) and the final optimized well geometry (`final_well_opt.xyz`) give as an ORCA input to NEB. Below is how your `orca.inp` should look for the NEB calculations:

```
! B3LYP 6-31G* NEB-TS freq

%maxcore 4000

%pal
nprocs 12
end

%NEB NEB_END_XYZFILE "final_well_opt.xyz"
END

* xyzfile 0 1 initial_well_opt.xyz
```

   - You want to ensure that the atom order matches between the initial and final .xyz file. Basically atom 1 in both files is C, atom 2 in both files is the same Hydrogen atom etc. If the atoms are not in the same order between .xyz files, NEB will fail. This is because NEB interpolates between the initial and the final .xyz file positions to find the transition state along that path.
   - When the NEB-TS ORCA calcualtion is finished, the transition state structure will be located in the file named "`orca_NEB-TS_converged.xyz`".

4. Take the transition state structure for each reaction and do an ORCA single point calculation using the same level of theory. Ensure you calculate vibrational frequencies as the zero point energy (ZPE) correction is calculated in this subroutine.

5. Create a table with total energy in kcal/mol of the minima and saddle points normalized to the energy of Well 2 (Formaldehyde). In the same table, report the total energies with the zero point energy (ZPE) correction applied in kcal/mol.

6. Use your prefered graphing code and create the potential energy surface graph (your results of Figure 1) without ZPE correction and with ZPE correction in kcal/mol. Ensure your energy values are normalized to Well 2 (Formaldehyde). You may add a label on the horizantal bars for each minima/maxima describing what structure it is (shown in Figure 1) and what relative energy it is located at. Note the x axis is an arbitrary axis and is called the Reaction Coordinate.

7. Visualize each minimum and saddle point structure and label the bond distances and any non-trivial bond angles directly on the image of the structure. You may use a visualization program or PowerPoint to organize and present these annotated structures clearly. There should be a total of nine structures to analyze in this step. Note: This task requires you to use the same analysis method that was applied in Assignment 1 - Part 1 - Step 6.

Grading Rubric:

Please include the scripts you used to generate the structures or information on where the structures were found, paths to where the calculations were ran on the HPC (a parent directory for this specific project works also) and your post processing scripts that generated the graphs and results in the Canvas Assignment submission. Including this information is the student's way of showing work in this class. If the information requested above is not provided, the instructor will assume plagaraism or collusion occured and respond accordingly.

The only accepted submission for the report is a MS Word document.

Criteria	**Points**
Structure generation	10
ORCA and NEB calculatons	30
Analysis of potential energy surfaces and minima/saddle point structures	50
Formatting and Submission of Word Document	5
Incusion of scripts and paths to calculations on HPC	5
Total	**100**

Citations

- Dallos, M.; Lischka, H.; Ventura Do Monte, E.; Hirsch, M.; Quapp, W. Determination of Energy Minima and Saddle Points Using Multireference Configuration Interaction Methods in Combination with Reduced Gradient Following: The S0 Surface of H2CO and the T1 and T2 Surfaces of Acetylene. Journal of computational chemistry 2002, 23 (5), 576-583. .